III.A.7 Advanced Fuel Cell Development

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Objectives

- Develop and validate advanced models for fuel cell analysis and design.
- Apply models for advanced fuel cell development.
- Transfer modeling capability to Solid State Energy Conversion Alliance (SECA) development teams and Core Technology Program participants.
- Analyze performance of solid oxide fuel cells (SOFCs) under dynamic loading.
- Develop capability to integrate computational fluid dynamics (CFD)-based fuel cell models with process models.
- Test perovskite coatings for fuel cell interconnects.

Approach

- Advance commercial CFD codes (FLUENT) to include fuel cell electrochemistry.
- Obtain model validation data using button cells representative of SECA technology.
- Apply new codes to investigate dynamics of SOFC operation.
- Integrate 3-D SOFC CFD model into process model of auxiliary power unit (APU).
- Apply doped $LaCrO_3$ coatings to standard interconnect material substrates and investigate coating properties and usefulness for SECA technologies.

Accomplishments

- First-generation fuel cell code has been released to SECA members (core and vertical teams).
- Model comparisons to button cell validation data have shown good agreement and have shown that specimen parameter changes (e.g., electrolyte thickness) can cause significant changes to model parameter values.
- Application of dynamic models has shown that circulating current conditions can exist within a cell/stack following certain common types of load changes.
- Developed capability to integrate FLUENT CFD models with Aspen Plus (Aspen Technology, Inc., Cambridge, MA) process simulation models.
- $LaCrO_3$ coatings were achieved having acceptable levels of area specific resistance (less that 0.1 ohm/cm^2) during short-term tests.

Future Directions

- Develop reforming capability within these advanced fuel cell models.
- Apply codes to investigate fuel cell design parameter sensitivity.

- Expand testing to include larger cells (e.g., 10 cm x 10 cm).
- Begin study of mechanical failure limitations of SOFC by developing high-temperature stain gage technology.
- Investigate mechanisms for silicon build-up under $LaCrO_3$-coated interconnects and determine if its oxide layer can be avoided or minimized through dopants.

Introduction

Because a fully functional hydrogen economy will take many years to create, the U.S. DOE is supporting the development of solid oxide fuel cells through the Solid State Energy Conversion Alliance (SECA) program as a way to efficiently use existing fossil fuel resources. The goal of this program is to provide low-cost fuel cell systems for mass markets. To achieve this goal will require new and innovative SOFC designs and materials. To assure success will require improved design tools and material data. The work performed here will address both needs by providing improved detailed modeling tools and new interconnect material options for SOFC design engineers.

Approach

Modeling

NETL has been developing fuel cell models using the FLUENT (Fluent Inc., Lebanon, NH) commercial software code. In this third phase (FY 2004) of development, further enhancements to the code allow for improved speed and accuracy in the analysis of cells and stacks by enabling the code to run in parallel mode on clusters of computers. In addition, internal reforming modeling capability will be added. This tool has been made available to SECA developers and to participants in the SECA Core Technology Program (Prinkey, 2004). To further improve the analysis of SECA and other fuel cell systems, NETL computational scientists, building on collaborations with NETL contracted activities, have developed the capability to integrate detailed FLUENT CFD models with Aspen Plus (Aspen Technology, Inc., Cambridge, MA) process simulation models (Zitney et al., 2004). Coupled CFD and process simulations provide a better understanding of the fluid mechanics that drive overall performance and efficiency of fuel cell systems. In addition, the analysis of the fuel cell using CFD is not done in isolation but within the context of the whole fuel cell process.

Dynamic Load Studies

Both model and experimental studies are used to investigate the performance of fuel cells under dynamic loads. It has already been made clear that the chemical kinetics at the cathode can degrade fuel cell performance (Jorgensen et al., 2000). While much about basic kinetics at the electrode/electrolyte interface is unknown, it can be expected that this is non-linear, thereby making the steady-state results from Jorgensen et al. incomplete. This project will examine these effects and compare to steady-state results to quantify any variances and to investigate cell properties that may change specifically resulting from dynamic loads.

Perovskite Interconnect Coatings

Use of lanthanum chromite coatings on metallic interconnect alloys may reduce the material costs for SOFC stacks considerably. This work will experimentally evaluate $LaCrO_3$-based coatings for application to SOFC systems. In FY 2004, we continued to study the film properties of $LaCrO_3$ films deposited by RF magnetron sputtering. We have also obtained Ca-doped $LaCrO_3$ thin films deposited by DC-magnetron sputtering on the Cr-containing stainless steel and nickel-based high-temperature alloy substrates (SS 446, Inconnel 600). After sputtering, the alloy samples with deposited film were annealed at 800×C for 2 hours. A number of analytical techniques (x-ray diffraction, scanning electron microscope, atomic force microscope, nanoindentation, Raman, and area specific resistance measurements) were used to characterize film properties such as phase formation, film morphology, mechanical properties and film resistance. We are also pursuing alternative low-cost methods of depositing chromite-based films, focusing at this point on dip-coating using "Pechini" solutions.

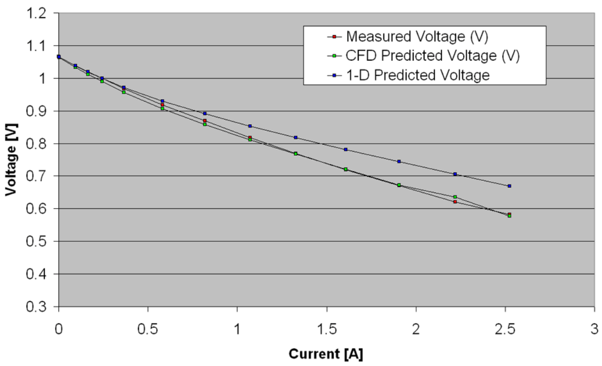

Figure 1. FLUENT Model Validation with Button Cell Data

Results

Modeling

Results from one of the validation studies of the new FLUENT SOFC model are shown in Figure 1. The results show very good agreement. To perform the validation effort, NETL has derived a consistent method for assessing the model parameters whereby the resistance of the electrolyte layer is first assessed based on measured cell data and resistivity data from the literature, followed by a calculated assessment of the exchange current from the data at low current density given an assumption of the contact resistance. Three loss mechanisms—electrolyte, cathode exchange current, and contact resistance—dominate the cell behavior.

Results from a detailed modeling study of a prototype short stack of SOFC cells operating in a crossflow configuration are shown in Figures 2-3. The study was used to demonstrate the present capability of the new model prior to release of the model to SECA partners in June of 2004. At this time, many SECA members (vertical and core) have downloaded the model, and NETL will continue to support their use of the model through updates and enhancements.

The Aspen Plus-FLUENT Integration Toolkit was applied to a SECA APU process simulation coupled with a 3-D planar SOFC CFD model. Detailed discussion of capability and results can be found in Zitney et al., 2004. This new capability is

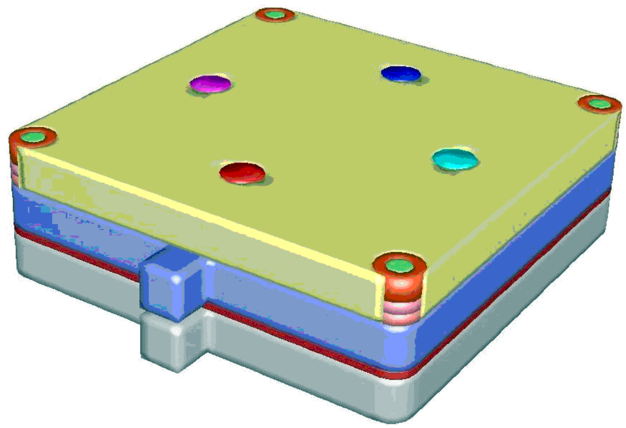

Figure 2. Test Case Geometry for FLUENT Model of an SOFC Cell

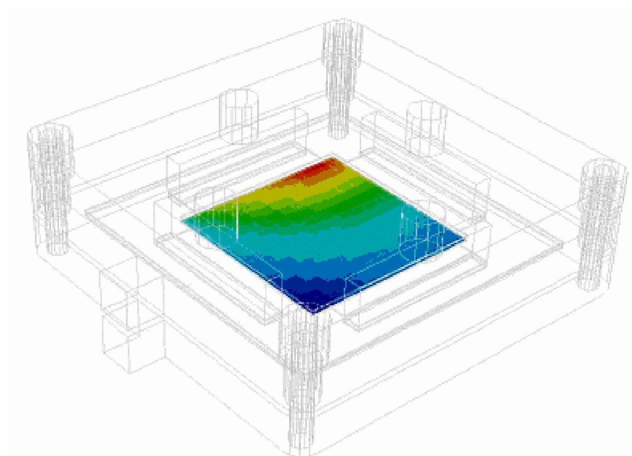

Figure 3. Sample FLUENT Model Results—Current Density Contour Plot

now available to help design and evaluate concepts for DOE's FutureGen program.

Dynamic Load Studies

The effect of applying transient loads on an SOFC cell was studied (Gemmen and Johnson, 2004). Some novel results are shown in Figure 4 for a representative "SECA technology" cell, showing the current density over the cell at the moment following load decrease. As can be seen, an internal current circulation condition can exist within the cell in spite of having lost external load. Such conditions are found to be due to temperature variations within the cell that control local Nernst voltages within the cell. With such variables driving potential conditions

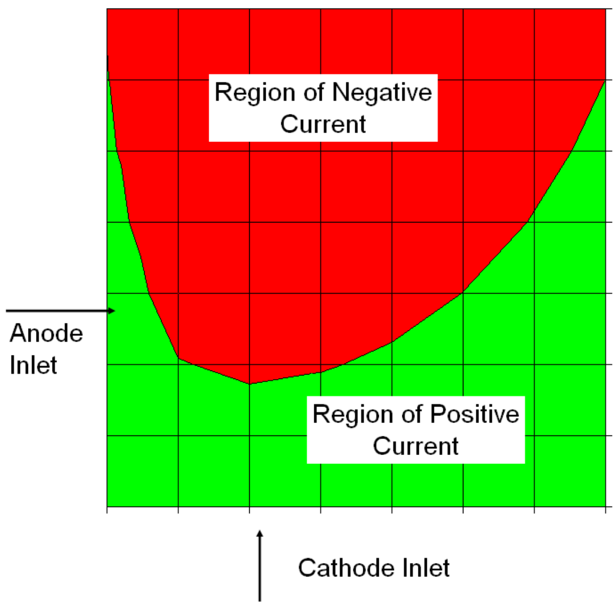

Figure 4. Cell Current Density Following Unload Event Showing Current Reversal

existing within the cell, an internal current circulation is produced. Such conditions have not been reported in prior work and may very well be of interest to SOFC designers who need to ensure that proper reducing and oxidizing conditions remain on the anode and cathode, respectively, at all times.

Perovskite Interconnect Coatings

We reported last year that the "as deposited" chromite films were amorphous as confirmed by x-ray diffraction (XRD). After annealing at 700°C for 1 hour, the amorphous film transformed to $LaCrO_3$ perovskite structure. Two transformations occurred during the amorphous-to-perovskite structure transition: the first is the amorphous-to-$LaCrO_4$ monoclinic structure transformation at 495°C, and the second is a $LaCrO_4$-to-$LaCrO_3$ orthorhombic structure transformation at 780°C (note that there is loss of oxygen in this transition). The second phase transition is accompanied by a fairly large volume decrease, which unfortunately results in the formation of porous structure for the $LaCrO_3$ perovskite thin film. Energy dispersive x-ray (EDS) analysis of the films prior to annealing showed that the "as deposited" film was oxygen-deficient relative to the chromite stoichiometry. This led us to anneal the films in a low partial pressure of oxygen, with the idea being that if we were far enough away from the composition of $LaCrO_4$, we could avoid the intermediate phase formation and thus obtain a denser film. XRD and AFM data indeed show that we have changed the reaction pathway and have obtained a smaller-grain, denser film. Further work is necessary to determine if we do in fact obtain a film that is dense enough to act as an adequate protective layer.

Resistivity measurements were carried out on a number of samples annealed both in air and in low oxygen partial pressure atmospheres. The results show initially that all samples have area specific resistances (ASR) at acceptable levels (less that 0.1 ohm/cm^2), with the low oxygen annealed sample initially performing the best. However, when the samples are exposed to air annealing for 100 hours, the ASR values increase, and the samples that were initially annealed in air become the best performers. We believe the reason for this is that the denser films change the kinetics of oxide growth under the perovskite layer to favor the formation of continuous silica layers (silica being present in most alloys as a trace element). Work is now being done to try and confirm this hypothesis.

Conclusions

Great progress is being made to provide new, advanced tools for fuel cell design. Basic model development is complete, with enhancements underway to add additional capabilities and enable integration with process models. These tools are now being validated using data from SOFC developers and from NETL test facilities. Collaboration with SECA developers and Core Technology participants is underway to validate the model and to provide the tools for their use. Validation of the model for single cells and cell stacks will be continued.

Insight to the dynamic behavior of SOFC systems is also being advanced. New fuel cell models that include the capability to calculate current reversal show that certain load transients can induce current circulation within the cell. Such conditions should be considered by fuel cell engineers during the design of these systems.

Finally, previous work on the perovskite films has shown the basic transformation behavior of $LaCrO_3$ perovskite coatings under conditions typical of SOFC operation. The understanding of these transformations has led us to change the annealing atmosphere to avoid detrimental intermediate phases. It was found that changing these processing conditions does improve film quality. ASR measurements, however, suggest that Si in the substrate alloys may be detrimental to conductivity of the film/substrate combination. Understanding of this problem is one aspect of future work. Work has also progressed to Ca-doped chromite films. Doping of the perovskite films is known to increase conductivity.

References

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2. Gemmen, R.S. and C. Johnson (2004), "Dynamics of Solid Oxide Fuel Cell Operation," Paper No. FUELCELL2004-2475, ASME Second International Conference on Fuel Cell Science, Engineering, and Technology, Eds. R. Shah and S.G. Kandlikar, Rochester NY, June 13-16, 2004, pp. 229-235.

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